SCIENCE FOR CERAMIC PRODUCTION

FORMATION OF MULLITE BASED ON HYDROMICA CLAY – ALUMINUM OXIDE COMPOSITIONS

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The results of studying mullite formation based on hydromica clay – $Al(OH)_3$ compositions are described. It is shown that formation of mullite (or a solid solution of mullite with corundum) is the most intense at temperatures of 1150 – 1200°C in compositions with a content of hydromica clay equal to 50 – 60%.

It is known [1, 2] that mullite in the binary system $Al_2O_3 – SiO_2$ is formed at temperatures over 1400°C with a molar ratio of $Al_2O_3 : SiO_2$ approximately equal to 1.5. The main results of studying the phase equilibrium of the $Al_2O_3 – SiO_2$ system can be reduced to the fact that the solid solution range extends from the composition corresponding to mullite $3Al_2O_3 \cdot 2SiO_2$ to the composition $2Al_2O_3 \cdot SiO_2$, i.e., the content of Al_2O_3 in solid mullite solutions reaches approximately 78%. In three- (or more) component systems containing K_2O, Na_2O, CaO, Fe_2O_3 (FeO), or TiO_2 the temperature of mullite formation decreases due to acceleration of reactions in the presence of a liquid phase emerging at a relatively low temperature. Formation of mullite or solid solutions of mullite with corundum in ternary systems occurs within a wide range adjacent to the binary line $Al_2O_3 – SiO_2$ and extending up to a K_2O (Na_2O) content equal to 20 – 25% [3]. Formation of mullite in aluminosilicate systems to a large extent is facilitated by Fe_2O_3 (FeO) dissolving up to 18 mol.% in mullite at a temperature of 1300°C [4].

Formation of mullite based on natural materials containing aluminum and silica, in particular argillaceous materials, depends mainly on the mineralogical composition, including the presence of argillaceous mineral — kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

Firing ceramics mixtures based on clays whose main argillaceous mineral is hydromica (illite), as a rule, produces the following new crystalline compounds: spinels $MgO \cdot Al_2O_3$ and $MgO \cdot Fe_2O_3$, feldspars $K(Na)[AlSi_3O_8]$, pyroxenes $Mg(Fe)Ca[Si_2O_6]$, quartz or cristobalite SiO_2.

Formation of mullite is registered only in single occasions, if the weight content in these clay reaches 17 – 19%.

Accordingly, formation of mullite in ceramic materials based on hydromica clays forming a liquid phase (at temperatures above 700°C) facilitating mullite formation is possible if an aluminum-bearing component is introduced in the respective mixtures.

This study describes the results of studying mullite formation from hydromica clay – $Al(OH)_3$ compositions. The hydromica clay in this case was Devonian clay from Latvia with the following chemical composition (wt.%): 5.0 ($K_2O + Na_2O$), 2.7 CaO, 3.2 MgO, 56.6 SiO_2 (+ TiO_2), 15.6 Al_2O_3, 7.0 Fe_2O_3, and the rest is calcination loss [5]. The mineralogical composition of clays is as follows (wt.%): 50 – 80 hydromica (illite), 5 – 15 kaolinite, 15 – 30 quartz, 2 – 6 calcite, and 5 – 9 goethite. The compositions considered are listed in Table 1.

The initial mixtures were homogenized and milled in planetary ball mills (average size of resulting particles 10 – 20 μm). Samples shaped as disks of diameter 35 and thickness 3.5 mm were produced by compression in a mold under pressure of 150 MPa. The samples were fired at a temperature of 1200°C for 2 h and also within a temperature interval of 1000 – 1200°C. After each firing cycle the ceramic properties were determined, such as water absorption, appa-

TABLE 1

Compo-sition	Mass content, %		Clay : $Al(OH)_3$ mass ratio
	hydromica clay	$Al(OH)_3$	
I	50	50	1.0 : 1.0
II	60	40	1.5 : 1.0
III	70	30	2.3 : 1.0
IV	80	20	4.0 : 1.0

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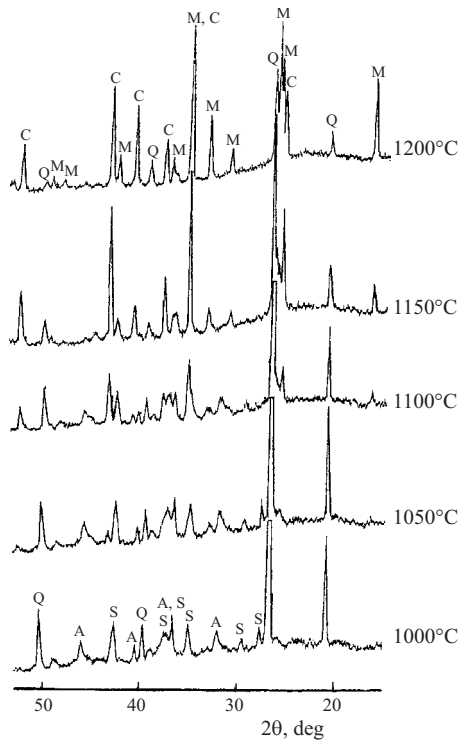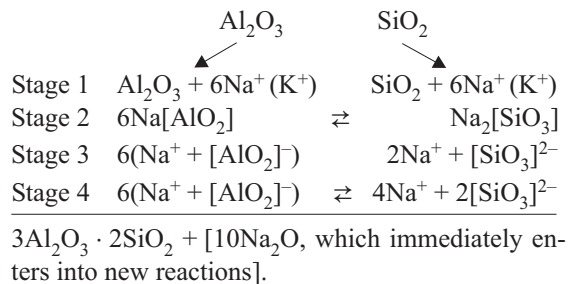
Fig. 1. Formation of crystalline phases depending on temperature in samples of composition II: A) γ-Al$_2$O$_3$; S) spinel; M) mullite; Q) quartz; C) α-Al$_2$O$_3$.
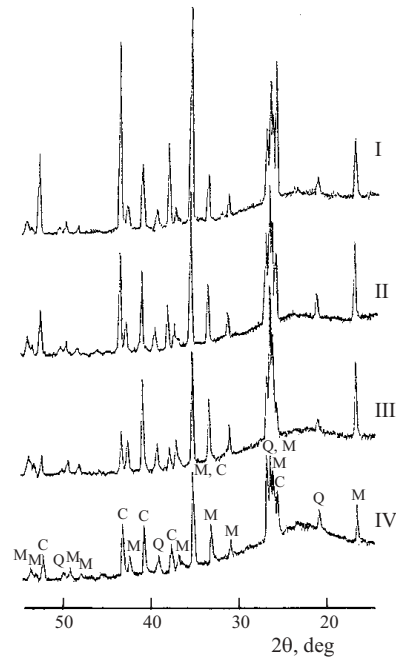

Fig. 2. Formation of crystalline phases at temperature 1200°C in samples of compositions I – IV: M) mullite; Q) quartz; C) α-Al$_2$O$_3$.

rent density, shrinkage (DIN-Normen 40685, Blatt 2/VDE 0335 Teil 2. 1974), and phase composition using the methods of x-ray diffraction analysis (DRON-3, Cu$_\alpha$ radiation) and microscopic analysis (MP EM-89 electron microscope, magnification × 1000).

The reactions of mullite formation on phase boundaries at about 1400°C can be schematically represented as follows:

$$Al_2O_3 \qquad SiO_2$$

Stage 1	$Al_2O_3 + 6Na^+ (K^+)$		$SiO_2 + 6Na^+ (K^+)$
Stage 2	$6Na[AlO_2]$	$\rightleftarrows$	$Na_2[SiO_3]$
Stage 3	$6(Na^+ + [AlO_2]^-)$		$2Na^+ + [SiO_3]^{2-}$
Stage 4	$6(Na^+ + [AlO_2]^-)$	$\rightleftarrows$	$4Na^+ + 2[SiO_3]^{2-}$

$3Al_2O_3 \cdot 2SiO_2 + [10Na_2O$, which immediately enters into new reactions].

The temperature of these reactions is approximately 700°C or higher, when hydromica loses consistency water and, accordingly, the structure of hydromica is substantially loosened. Starting at that moment, an insignificant quantity of a liquid phase is formed, and reactions (steps 1 and 2) start, presumably with formation of metaaluminate and metasilicate. As the quantity of the liquid phase increases due to melting of Na$_2$[SiO$_3$], at a temperature about 850°C reactions between ions Na$^+$–AlO$_2^-$ and Na$^+$–SiO$_3^{2-}$ take

place with formation of mullite seeds. A catalytic effect is also exercised by iron and titanium ions (present in hydromica minerals) and the high degree of dispersion of argillaceous particles.

It can be seen in Fig. 1 that the formation of new phases identified by x-ray phase analysis in hydromica clay – Al(OH)$_3$ compositions (for instance in the mixture with 60% clay + 40% Al(OH)$_3$) starts after decomposition of components and formation of the liquid phase and is especially intense in a temperature interval of 1000 – 1200°C, when new phases emerge: spinel: Mg(Fe^{2+})[AlO$_4$], γ-Al$_2$O$_3$, corundum (or solid solution of corundum and mullite), and mullite, quartz being the predominant impurity phase. Formation of mullite intensifies within a temperature interval of 1150 – 1200°C. It is known [6] that mullite, which has the rhombohedral habitus, frequently contains excessive Al$_2$O$_3$, furthermore, the presence of OH ions and fluorine is possible. The presence of impurity ions is assumed, which incorporate into the octahedral vacancies in the structure of emerging mullite.

Judging by variations in the diffraction maximum intensities in samples of composites I – IV (Table 1) fired at 1200°C for 2 h, the most intense mullite formation occurs in mixtures with mass ratio between the two components ranging from 1.0 : 1.0 to 1.5 : 1.0, i.e., with 40 – 50% content of Al(OH)$_3$ (Fig. 2).

The development of microstructure in samples of compositions I – IV formed at 1200°C is shown in Fig. 3. It can be seen that with increasing ratio of clay to Al(OH)$_3$, ceramic materials become more amorphous, which is indicated by a
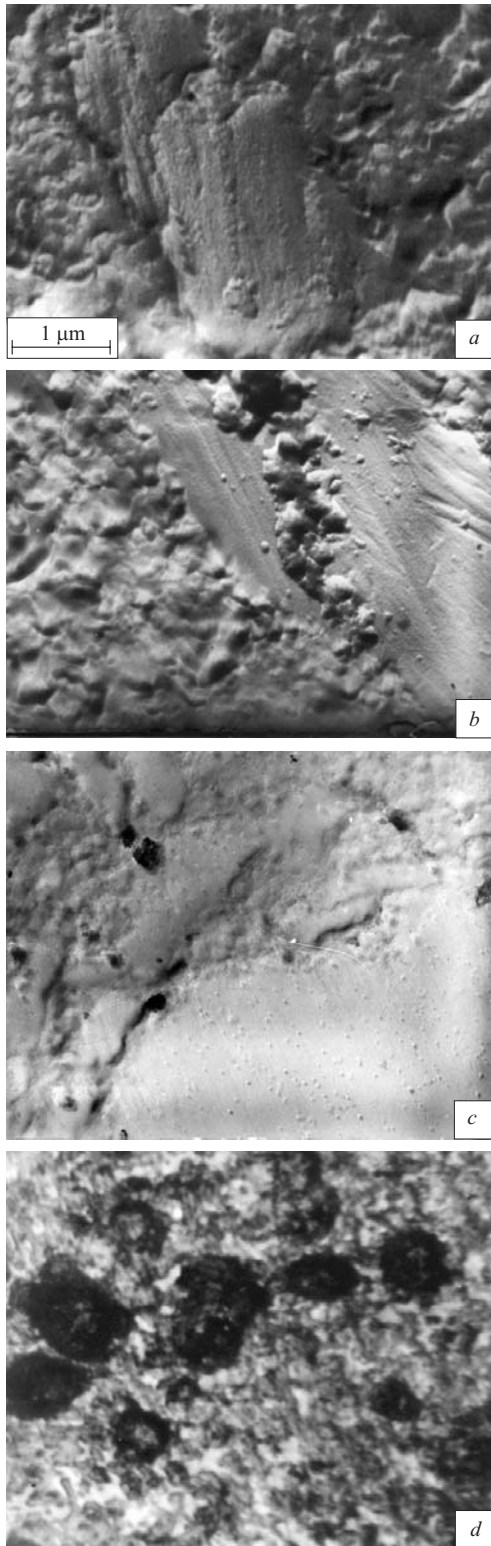
Fig. 3. Microphotos of samples of compositions I (*a*), II (*b*), III (*c*), and IV (*d*) fired at 1200°C.

Fig. 4. Dependence of water absorption and apparent density on temperature in samples of compositions I – IV.

perceptible decrease in water absorption of fired samples (Fig. 4). Samples with initial ratio of clay to Al(OH)$_3$ equal to 4 : 1 (Fig. 3*d*) rounded pores are clearly visible, which is
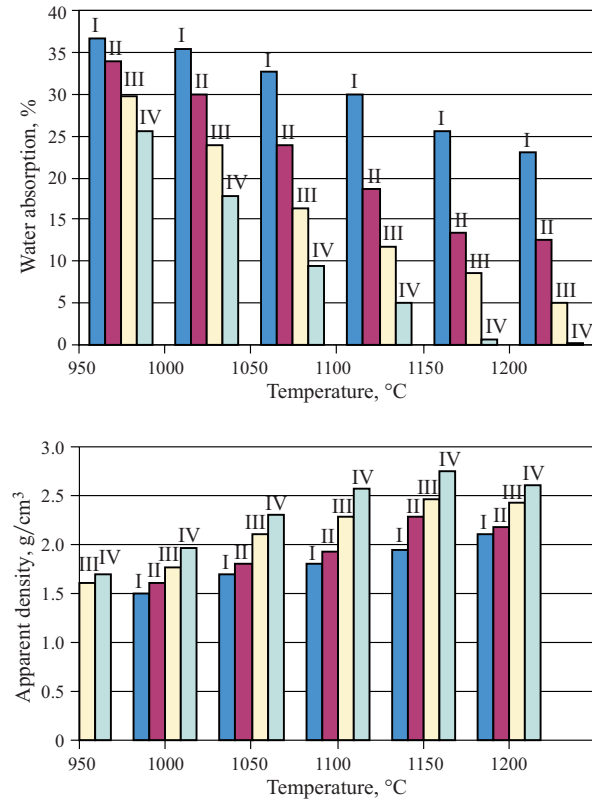
evidence of not only the degree of sintering of materials but also the presence of a substantial quantity of liquid phase in the firing process, which facilities the transformation Fe^{3+} → Fe^{2+} in the argillaceous component of material and additional formation of pores (as evidenced by the decrease in apparent density).

The microstructure of ceramic samples made of mixtures with a clay to Al(OH)$_3$ ratio ranging from 1.0 : 1.0 to 1.5 : 1.0 passes from amorphous to a crystalline one. The well-extended crystals of prismatic habitus (Fig. 3*a*) are presumably mullite crystals.

To conclude it should be noted that formation of mullite (or solid solutions of mullite with corundum) based on hydromica clay – Al(OH)$_3$ compositions proceeds most intensely at temperatures 1150 – 1200°C in compositions with a hydromica component content equal to 50 – 60%. Such clay content facilitates the formation of an optimum quantity of liquid phase in firing (starting with around 700°C) and simultaneous reactions of mullite formation due to previously formed (at about 1000°C) crystalline nuclei, i.e., spinel, corundum, and quartz. The most intense mullite formation occurs at 1150 – 1200°C. Compared to the known process of mullite formation from oxides [7] at about 1400°C, the temperature in our study was reduced by 150 – 200°C.

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